Method of Envelope Functions and Intervalley Γ-X_z Interaction of States in (001) III-V Semiconductor Heterostructures

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Abstract

The $\mathbf{k} \cdot \mathbf{p}$ method is used to analyze the problem of intervalley Γ-X_z interaction of conduction band states in (001) lattice-matched III-V semiconductor heterostructures. A convenient basis for expansion of the wave function is systematically selected and a multi-band system of equations is derived for the envelope functions which is then reduced to a system of three equations for three valleys (Γ_1, X_1, and X_3) by using a unitary transformation. Intervalley Γ-X_z mixing is described by short-range potentials localized at heterojunctions. The expressions for the parameters determining Γ-X_z mixing strength explicitly contain the chemical composition profile of the structure, so mixing is naturally stronger for abrupt heterojunctions than for structures with a continuously varying chemical composition. It is shown that the direct Γ_1-X_1 interaction of comparable strength to Γ_1-X_3 interaction exists. This must be taken into account when interpreting tunnel and optical experiments since X_1 valley is substantially lower in energy than X_3 valley.

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1   Introduction

Heterostructures with quantum wells and barriers based on GaAs/AlGaAs are popular objects for studying the physical processes accompanying resonant tunneling and optical transitions. These structures are particularly interesting because in GaAs the minimum of the conduction band is situated at the center of the first Brillouin zone (Γ_1 symmetry) whereas the minimum of the AlAs conduction band lies near X point where the bands having X_1 and X_3 symmetry are close together, X_1 band being the principal one (X_3

band is 350 meV higher energy). On each cubic axis, there is a pair of X valleys, one from X_1 band and one from X_3 band. Layers with predominantly Ga content act as barriers for X electrons while regions with Al predominating act as barriers for Γ electrons. Under certain conditions, resonant tunneling interaction can take place between energetically close states of Γ and X valleys, and this is observed on the current-voltage characteristics even of single-barrier structures (see, e.g., Refs. [1, 2]) and also in optical experiments [3, 4]. The conditions for the existence of this interaction generally involve the presence of structural defects, impurities, heterojunction roughness, and/or interaction with short-wavelength phonons. However, in (001) heterostructures, interaction of Γ valley with X_z valleys (i.e, X valleys lying on the quasi-momentum axis directed along the normal to the surface) is caused by the potential of the structure itself which leads to non-conservation of the quasi-momentum component k_z perpendicular to the junction. As a result of size quantization for fairly thin (less than 50 Å) AlGaAs layers, X_z-valley states are situated below all X valleys so that an analysis of Γ-X_z interaction at the heterojunction is important for an accurate description of Γ-X transitions [5].

This type of intervalley mixing has been studied theoretically both phenomenologically [6] and using a tight-binding model [7, 8], and also using a pseudo-potential method [9]. Nevertheless, the level of understanding of the processes leading to Γ-X_z mixing of electronic states is far from satisfactory. For instance, the results of Ref. [8, 9] indicate that the direct Γ_1-X_1 interaction is extremely weak and Γ-X_z mixing is merely attributable to Γ_1-X_3 interaction, whereas, according to Ref. [7], Γ_1-X_1 interaction is the determining factor (however, the parameters of the tight-binding model used in Ref. [7] are such that X_3 band is very high in terms of energy and is in fact eliminated from the analysis). Studies [10, 11], in which the form of Γ-X_z interaction potential was determined by direct calculations of the matrix elements of the model heterointerface potential using the complete wave functions of the states also give a contradictory answer to the question of the strength of Γ_1-X_1 interaction. According to the results of Ref. [10], this interaction is weak whereas the results of Ref. [11] suggest the opposite: the strength of Γ_1-X_1 mixing can be comparable to those of Γ_1-X_3 mixing. The solution of this problem is important for interpreting tunneling and optical experiments since Γ_1-X_1 transitions are usually observed experimentally.

In the present study Γ-X_z interaction (mixing) is analyzed using the method of envelope functions. This is a fairly explicit technique which does not have the disadvantage of the tight-binding model in which the heterointerface is oversimplified, while calculations using the empirical pseudo-potential method are much more cumbersome than those using the envelope function method. Note that so far attempts to derive a system of equations for the envelope functions jointly describing Γ and X states have not produced satisfactory results. This is mainly because an atomically abrupt change in the crystal potential at the heterojunctions produces Γ-X_z mixing [12], and correct allowance for such abrupt changes in the potential is outside the scope of the usual method of Luttinger-Kohn envelope functions. In Refs. [10, 11], in which the problem was analyzed using the envelope function method, Γ-X interaction was analyzed using perturbation theory, but as a basis there was selected a generally over-full set

corresponding to the set of Kohn-Luttinger functions for Γ and X states. An over-full (and nonorthogonal) basis can, in principle, give an erroneous result. In addition, this approach cannot be applied directly to describe the states of the continuous spectrum which is important for Γ-X_z tunneling problem. Nevertheless, the results of the present study agree qualitatively with the conclusions of Ref. [11].

The problem of adequate description of intervalley mixing of states in heterostructures is similar to the problem of intervalley splitting of impurity states in multi-valley semiconductors (for example, in Si and Ge). It is known, see Ref. [13], that allowance for the short range part of the impurity potential ("the correction to the central cell") not only yields a "chemical shift" of the impurity-state energy but also lifts the valley degeneracy. In Ref. [14], we proposed a fairly simple method of analyzing heterojunctions with an atomically abrupt change in chemical composition. This method involves isolating the "smooth" component of the heterostructure potential and the "sharp" component which is only nonzero near the heterojunction. The smooth component is "processed" by a standard technique (the Kohn-Luttinger method) while the sharp component is considered as a correction to the central cell. In Ref. [14] we only considered states near Γ point in the Brillouin zone and in the present study we develop the method further to describe the interaction of states near different points in $\mathbf{k}$ space. These results were first presented at the III All-Russia Conference on the Physics of Semiconductors, see [15], and also [16].

2 Formalism of the Envelope Function Method

2.1 Formulation of the Problem

We shall consider the electron states in (001) III-V heterostructures formed from related lattice-matched (with the lattice constant a) semiconductors having zinc blende symmetry. By related structural materials we understand fairly small band offsets so that in the energy range of interest the conduction band states near Γ point can be described using a single-band variant and the states near the point X can be described using two-band (for X_1 and X_3 bands) variants of the envelope function method. We shall also assume that the energy gap between the states of interest to us in the Γ and X valleys is smaller than or of the order of the band offset. This means that we can consider the direct interaction of Γ_1, X_1, and X_3 states "exactly" and interaction via all other bands can be taken into account using perturbation theory. Since the desired Hamiltonian of the equation for the envelope functions should depend explicitly on the number of monoatomic layers of each material forming the structure [7, 17], we shall consider a structure with two symmetric heterojunctions as the simplest case to obtain this dependence. For simplicity, we shall neglect spin-orbit interaction and also external smooth potentials. The single-electron Schrödinger equation then has the following form:

$$\left(\frac{\mathbf{p}^2}{2m_0} + U \right) \Psi\left(\mathbf{r}\right) = \epsilon \Psi\left(\mathbf{r}\right). \tag{1}$$

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Here m_0 is the free electron mass, $\mathbf{p}$ is the momentum operator, and $U \equiv U(\mathbf{r})$ is the crystal potential of the heterostructure. We shall first use the following model for this potential (a more realistic situation will be discussed in Section 3):

$$U = U_1 + P(z)[U_2 - U_1] \equiv U_1 + P(z)\,\delta U, \tag{2}$$

and $U_1 \equiv U_1(\mathbf{r})$ and $U_2 \equiv U_2(\mathbf{r})$ are periodic (continued to all space) potentials of the two heterostructure materials, the z-axis is perpendicular to the heterojunction plane; the form-factor $P(z)$ of the heterostructure having the heterointerfaces at $z = 0$ and $z = L$ is defined so that

$$P(z) = \begin{cases} 0, & z < -d; \\ 1, & d < z < L - d; \\ 0, & z > L + d. \end{cases} \tag{3}$$

The behavior of the function $P(z)$ in the transition regions (of width $2d$ each) near the heterointerfaces may be fairly arbitrary. Here, the symmetry of the structure implies that $P(z) = P(L - z)$, $L > d$. We shall assume that the layer of width L contains an integer number of monolayers: $L = \mathcal{N}a/2$, where $\mathcal{N}$ is a natural number.

2.2 Choice of Complete Orthonormalized Set of Basis Functions

As in Ref. [14], the potential $P(z)\delta U$ is analyzed in terms of perturbation theory and the complete and orthonormalized set of functions used to expand the complete wave function $\Psi(\mathbf{r})$ is constructed of Bloch functions of the base semiconductor (having the crystal potential U_1). In our case, the most natural basis is a mixed basis of Kohn-Luttinger functions for the points Γ and X_z. In order to make this set complete and orthonormalized, it should be constructed as follows. We first expand $\Psi(\mathbf{r})$ in terms of the Bloch functions $u_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\mathbf{r}}$ of the base crystal which correspond to the energy eigenvalues $\epsilon_{n\mathbf{k}}$, where n and $\mathbf{k}$ are the band index and the quasi-momentum vector, respectively:

$$\Psi(\mathbf{r}) = \sum_{n'} \int \mathcal{A}_{n'}(\mathbf{k}')\, e^{i\mathbf{k}'\mathbf{r}} u_{n'\mathbf{k}'}\, d^3k'. \tag{4}$$

Summation in (4) is performed over all bands and integration is performed over the region Λ_0 nonequivalent $\mathbf{k}$. In order not to consider two equivalent X_z points (having the coordinates $(0, 0, 2\pi/a)$ and $(0, 0, -2\pi/a)$ in $\mathbf{k}$ space), we shall not operate in the first Brillouin zone constructed as a Wigner-Seitz cell but we shall define a region Λ_0 such that points Γ and, for example, $\mathbf{q} = (0, 0, 2\pi/a)$ are contained in this region with their vicinities. Following Ref. [13] (Sec. 7-3), we divide Λ_0 into two subregions Λ_Γ and $\tilde{\Lambda}_X$ containing the points Γ and X_z with their vicinities, where $\Lambda_\Gamma \cup \tilde{\Lambda}_X = \Lambda_0$ and $\Lambda_\Gamma \cap \tilde{\Lambda}_X = 0$ (see comments on this method of division in Section 2.4). Now, following Ref. [18] we use series expansions of the periodic function $u_{n\mathbf{k}}$:

$$u_{n\mathbf{k}} = \sum_{m'} b_{m'n}(\mathbf{k})\, u_{m'0}, \quad u_{n\mathbf{k}} = \sum_{m'} c_{m'n}(\mathbf{k})\, u_{m'\mathbf{q}}.$$

Then (4) can be rewritten in the following form:

$$\Psi\left(\mathbf{r}\right) = \sum_{n',m'} \int_{\mathbf{k}'\in\Lambda_\Gamma} \mathcal{A}_{n'}\left(\mathbf{k}'\right) b_{m'n'}\left(\mathbf{k}'\right) e^{i\mathbf{k}'\mathbf{r}} u_{m'0}\, \mathrm{d}^3 k' +$$

$$+ \sum_{n',m'} \int_{\mathbf{k}'+\mathbf{q}\in\tilde{\Lambda}_X} \mathcal{A}_{n'}\left(\mathbf{k}'+\mathbf{q}\right) c_{m'n'}\left(\mathbf{k}'+\mathbf{q}\right) e^{i\mathbf{k}'\mathbf{r}} e^{i\mathbf{q}\mathbf{r}} u_{m'\mathbf{q}}\, \mathrm{d}^3 k'. \tag{5}$$

We then define the functions

$$\mathcal{F}_{m'}^{(\Gamma)}\left(\mathbf{k}'\right) = \sum_{n'} \mathcal{A}_{n'}\left(\mathbf{k}'\right) b_{m'n'}\left(\mathbf{k}'\right), \tag{6}$$

$$\mathcal{F}_{m'}^{(X)}\left(\mathbf{k}'\right) = \sum_{n'} \mathcal{A}_{n'}\left(\mathbf{k}'+\mathbf{q}\right) c_{m'n'}\left(\mathbf{k}'+\mathbf{q}\right), \tag{7}$$

which will specifically comprise the envelopes of the functions of Γ and X_z states in $\mathbf{k}$ representation, and we shall define the region Λ_X such that the condition $\mathbf{k} \in \Lambda_X$ is satisfied for all $\mathbf{k} + \mathbf{q} \in \tilde{\Lambda}_X$ (shift of the origin in $\mathbf{k}$ space). Now (5) can have the form of an expansion of $\Psi\left(\mathbf{r}\right)$ in terms of a complete set of Kohn-Luttinger functions near the points Γ and X_z:

$$\Psi\left(\mathbf{r}\right) = \sum_{m'} \int_{\Lambda_\Gamma} \mathcal{F}_{m'}^{(\Gamma)}\left(\mathbf{k}'\right) \chi_{m'\mathbf{k}'}^{(\Gamma)}\, \mathrm{d}^3 k' + \sum_{m'} \int_{\Lambda_X} \mathcal{F}_{m'}^{(X)}\left(\mathbf{k}'\right) \chi_{m'\mathbf{k}'}^{(X)}\, \mathrm{d}^3 k' =$$

$$= \sum_{v'=\Gamma,X} \sum_{m'} \int_{\Lambda_{v'}} \mathcal{F}_{m'}^{(v')}\left(\mathbf{k}'\right) \chi_{m'\mathbf{k}'}^{(v')}\, \mathrm{d}^3 k', \tag{8}$$

where the Kohn-Luttinger functions are

$$\chi_{m\mathbf{k}}^{(\Gamma)} = e^{i\mathbf{k}\mathbf{r}} u_{m0} \equiv e^{i\mathbf{k}\mathbf{r}} \phi_m^{(\Gamma)}, \quad \chi_{m\mathbf{k}}^{(X)} = e^{i\mathbf{k}\mathbf{r}} e^{i\mathbf{q}\mathbf{r}} u_{m\mathbf{q}} \equiv e^{i\mathbf{k}\mathbf{r}} \phi_m^{(X)}.$$

Thus, the Fourier transforms of the envelope functions constructed above differ from the usual ones [18] only in terms of the domains of their definition. In our case, these are the regions Λ_Γ (for states near the center of the Brillouin zone) and Λ_X (for states near X_z point) rather than the complete first Brillouin zone.

For simplicity, below we shall also assume that $\phi_m^{(v)}$ are real. Taking the following orthonormalization relationship for the Bloch functions:

$$\int_{\substack{all \\ space}} u_{n'\mathbf{k}'}^* e^{-i\mathbf{k}'\mathbf{r}} u_{n\mathbf{k}} e^{i\mathbf{k}\mathbf{r}}\, \mathrm{d}^3 r = \delta_{nn'}\delta\left(\mathbf{k}-\mathbf{k}'\right), \tag{9}$$

we obtain the required orthonormalization relationship for the basis functions [18]:

$$\int_{\substack{all \\ space}} \left(\chi_{n'\mathbf{k}'}^{(v')}\right)^* \chi_{n\mathbf{k}}^{(v)}\, \mathrm{d}^3 r = \delta_{vv'}\delta_{nn'}\delta\left(\mathbf{k}-\mathbf{k}'\right). \tag{10}$$

2.3 Multi-band System of $\mathbf{k} \cdot \mathbf{p}$ Equations

In the basis specified above the procedure for obtaining $\mathbf{k} \cdot \mathbf{p}$ system of equations is trivial, see [18]. Using the expansion (8) in (1), multiplying both sides of the equation by $(\chi_{m\mathbf{k}}^{(v)})^*$ and integrating over all $\mathbf{r}$ space, we obtain the following system of equations:

$$\left(\epsilon_m^{(v)} + \frac{\hbar^2 \mathbf{k}^2}{2m_0}\right) \mathcal{F}_m^{(v)}(\mathbf{k}) + \sum_{m'} \frac{\hbar \mathbf{p}_{mm'}^{(v)} \cdot \mathbf{k}}{m_0} \mathcal{F}_{m'}^{(v)}(\mathbf{k}) +$$

$$+ \sum_{v'=\Gamma,X} \sum_{m'} \int_{\Lambda_{v'}} \mathcal{M}_{mm'}^{(vv')}(\mathbf{k},\mathbf{k}') \mathcal{F}_{m'}^{(v')}(\mathbf{k}') \, \mathrm{d}^3 k' = \epsilon \mathcal{F}_m^{(v)}(\mathbf{k}). \tag{11}$$

Here $\epsilon_m^{(\Gamma)} = \epsilon_{m0}$ and $\epsilon_m^{(X)} = \epsilon_{m\mathbf{q}}$,

$$\mathbf{p}_{mm'}^{(v)} = \langle m, v \mid \mathbf{p} \mid m', v \rangle \equiv \frac{(2\pi)^3}{\Omega} \int_{\text{cell}} \phi_m^{(v)} \mathbf{p} \phi_{m'}^{(v)} \, \mathrm{d}^3 r,$$

$\langle m, v \mid \mathbf{p} \mid m', v' \rangle = 0$ for $v \neq v'$, and Ω is the unit cell volume, and

$$\mathcal{M}_{mm'}^{(vv')}(\mathbf{k},\mathbf{k}') = \int_{\substack{all \\ space}} e^{-i(\mathbf{k}-\mathbf{k}')\mathbf{r}} \phi_m^{(v)} P(z) \, \delta U \phi_{m'}^{(v')} \, \mathrm{d}^3 r.$$

The matrix elements $\mathcal{M}_{mm'}^{(vv')}(\mathbf{k},\mathbf{k}')$ were analyzed in Ref. [14]. It was shown that the contribution of the perturbation potential can be divided into "smooth" and "sharp" components (the latter is exponentially small for smooth perturbations on the scale a). The contribution of the sharp component is a correction to that of the smooth component (for the case when the width of the heterostructure layers is much greater than a), and it can be written in the form of converging series in powers of $(k_z - k_z')$. We will use the effective-mass approximation with spatially independent effective-mass parameters and we will only allow for the effects of abruptness of the heterojunctions in the first order in terms of the parameter $a\bar{k}_z$ [14, 19], where $\bar{k}_z$ is the characteristic quasi-momentum of the state. We shall consider the intervalley elements $\mathcal{M}_{mm'}^{(vv')}(\mathbf{k},\mathbf{k}')$, $v \neq v'$ in greater detail and for $\mathcal{M}_{mm'}^{(vv)}(\mathbf{k},\mathbf{k}')$, following Ref. [14, 19], we obtain

$$\mathcal{M}_{mm'}^{(vv)}(\mathbf{k},\mathbf{k}') = \left[\mathcal{P}(k_z - k_z') \, \delta U_{mm'}^{(v)} + \frac{1}{2\pi} \sum_{j \neq 0} \frac{\langle m, v \mid \delta U e^{iK_j z} \mid m', v \rangle}{iK_j} \times \right.$$

$$\left. \times \left(\int_{-d}^{d} P'(z) e^{-iK_j z} \mathrm{d}z - e^{-i(k_z - k_z')L} \int_{-d}^{d} P'(z) e^{iK_j z} \mathrm{d}z \right) \right] \delta\left(\mathbf{k}_\| - \mathbf{k}_\|'\right). \tag{12}$$

Here we introduce the notation: $\mathcal{P}(k_z)$ is the Fourier transform of the function $P(z)$; the matrix element $\delta U_{mm'}^{(v)} = \langle m, v \mid \delta U \mid m', v \rangle$; $K_j = (4\pi/a)j$, and j is an integer; $P'(z) = \mathrm{d}P(z)/\mathrm{d}z$; and $\mathbf{k}_\| = (k_x, k_y, 0)$. We used the symmetry $P(z) = P(L - z)$, and also the fact that $e^{iK_j L} = 1$. Here, we give all the matrix elements (12) required subsequently. We assign the indices 'w', 'u' and 'v' to the conduction-band states Γ_1, X_1 and X_3,

respectively, and omit the valley indices since the band index in our approximation now uniquely defines the state. Using symmetry concepts we obtain

$$\mathcal{M}_{ss}\left(\mathbf{k}, \mathbf{k}'\right) = \left[\mathcal{P}\left(k_z - k_z'\right)\delta U_{ss} + \frac{1}{2\pi}d_{ss}\left(1 + e^{-i(k_z - k_z')L}\right)\right]\delta\left(\mathbf{k}_\| - \mathbf{k}_\|'\right),$$

where $s = $ w, u, v; and the parameters d_{ss} are determined as follows:

$$d_{ss} = -\sum_{j \neq 0}\frac{\langle s \mid \delta U \cos\left(K_j z\right) \mid s \rangle}{K_j}\int_{-d}^{d} P'(z)\sin\left(K_j z\right)\mathrm{d}z.$$

The potential also makes a contribution to the direct interaction of X_1 and X_3 states:

$$\mathcal{M}_{\mathrm{uv}}\left(\mathbf{k}, \mathbf{k}'\right) = \frac{1}{2\pi}d_{\mathrm{uv}}\left(1 - e^{-i(k_z - k_z')L}\right)\delta\left(\mathbf{k}_\| - \mathbf{k}_\|'\right),$$

where

$$d_{\mathrm{uv}} = \sum_{j \neq 0}\frac{\langle \mathrm{u} \mid \delta U \sin\left(K_j z\right) \mid \mathrm{v} \rangle}{K_j}\int_{-d}^{d} P'(z)\cos\left(K_j z\right)\mathrm{d}z.$$

We shall now consider the most interesting to us intervalley matrix elements $\mathcal{M}_{mm'}^{(vv')}$, $v \neq v'$:

$$\mathcal{M}_{mm'}^{(\Gamma X)}\left(\mathbf{k}, \mathbf{k}'\right) = \int_{\substack{all \\ space}} P(z)\,e^{-i(\mathbf{k} - \mathbf{k}' - \mathbf{q})\mathbf{r}}u_{m0}\delta U u_{m'\mathbf{q}}\,\mathrm{d}^3 r.$$

We shall analyze this matrix element using the same method which yielded (12). We shall use an expansion of the periodic function $u_{m0}\delta U u_{m'\mathbf{q}}$ as a Fourier series which gives

$$\mathcal{M}_{mm'}^{(\Gamma X)}\left(\mathbf{k}, \mathbf{k}'\right) = \sum_l C_l^{m(\Gamma)m'(X)}\mathcal{P}\left(k_z - k_z' - q_z + K_{zl}\right)\delta\left(\mathbf{k}_\| - \mathbf{k}_\|' + \mathbf{K}_{\|l}\right), \qquad (13)$$

where $\mathbf{K}_l \equiv (K_{zl}, \mathbf{K}_{\|l})$ are the vectors of the reciprocal lattice, and

$$C_l^{m(\Gamma)m'(X)} = \frac{(2\pi)^3}{\Omega}\int_{\mathrm{cell}} u_{m0}\delta U e^{i\mathbf{K}_l\mathbf{r}}u_{m'\mathbf{q}}\mathrm{d}^3 r \equiv \left\langle m, \Gamma \mid \delta U e^{i(\mathbf{K}_l - \mathbf{q})\mathbf{r}} \mid m', X \right\rangle.$$

As was shown in Ref. [19], for the region where $|k_x| + |k_y| < \pi/a$, whose size is fairly large for our purposes [we obviously used this constraint in the derivation of (12)], only the vectors of the reciprocal lattice with $\mathbf{K}_{\|l} = 0$ will contribute to (13):

$$\mathcal{M}_{mm'}^{(\Gamma X)}\left(\mathbf{k}, \mathbf{k}'\right) = \sum_j \left\langle m, \Gamma \mid \delta U e^{i(K_j - q_z)z} \mid m', X \right\rangle\mathcal{P}\left(k_z - k_z' + K_j - q_z\right)\delta\left(\mathbf{k}_\| - \mathbf{k}_\|'\right) =$$

$$= \sum_{j = \pm 1, \pm 3, \pm 5, \dots} \left\langle m, \Gamma \mid \delta U e^{i\frac{2\pi}{a}jz} \mid m', X \right\rangle\mathcal{P}\left(k_z - k_z' + \frac{2\pi}{a}j\right)\delta\left(\mathbf{k}_\| - \mathbf{k}_\|'\right). \qquad (14)$$

We shall analyze the function $\mathcal{P}(k_z - k_z' + (2\pi/a)j)$, contained in (14) in greater detail:

$$\mathcal{P}\left(k_z - k_z' + \frac{2\pi}{a}j\right) = \frac{1}{2\pi i}\frac{1}{k_z - k_z' + \frac{2\pi}{a}j}\int_{-\infty}^{+\infty} P'(z)\,e^{-i\left(k_z - k_z' + \frac{2\pi}{a}j\right)z}\,\mathrm{d}z =$$

$$= \frac{1}{2\pi i} \frac{1}{k_z - k_z' + \frac{2\pi}{a}j} \left(\int\limits_{-d}^{d} P'(z) \, e^{-i\frac{2\pi}{a}jz} e^{-i(k_z - k_z')z} \, \mathrm{d}z - \right.$$

$$\left. -e^{-i(k_z - k_z')L} e^{-i\frac{2\pi}{a}jL} \int\limits_{-d}^{d} P'(z) \, e^{i\frac{2\pi}{a}jz} e^{i(k_z - k_z')z} \, \mathrm{d}z \right),$$

where we again used the property $P(z) = P(L-z)$. We now expand $(k_z - k_z' + (2\pi/a)j)^{-1}$, $\exp(-i(k_z - k_z')z)$, and $\exp(i(k_z - k_z')z)$ as series in powers of $(k_z - k_z')$, where the convergence of the first series is ensured by the property $\mid k_z - k_z' \mid < 2\pi/a$, since $\mathbf{k} \in \Lambda_\Gamma$ and $\mathbf{k}' \in \Lambda_X$. We only retain the first terms of these expansions. This gives a good approximation for $\bar{k}_z \ll 2\pi/a$ and $\bar{k}_z \ll 1/(2d)$, where $\bar{k}_z$ is the characteristic quasi-momentum of the state or the reciprocal characteristic length of variation of the envelope functions (6) and (7) in $\mathbf{r}$ representation (i.e., the envelope functions should vary weakly on scales of order a and on scales of the order of the widths of the interface regions). Now, bearing in mind that for all values of the summation index j in (14) $\exp(-2\pi ijL/a) = (-1)^{\mathcal{N}}$, we obtain:

$$\mathcal{P}\left(k_z - k_z' + \frac{2\pi}{a}j\right) = \frac{1}{2\pi i} \frac{a}{2\pi j} \left(\int\limits_{-d}^{d} P'(z) \, e^{-i\frac{2\pi}{a}jz} \, \mathrm{d}z - \right.$$

$$\left. -(-1)^{\mathcal{N}} e^{-i(k_z - k_z')L} \int\limits_{-d}^{d} P'(z) \, e^{i\frac{2\pi}{a}jz} \, \mathrm{d}z \right).$$

Here, there is a dependence of the effective potential on the number of monoatomic layers $\mathcal{N}$, which mixes the valley states assigned to different points in $\mathbf{k}$ space. We now write the matrix elements we require (we again drop the valley index):

$$\mathcal{M}_{\mathrm{wu}}(\mathbf{k}, \mathbf{k}') = \frac{1}{2\pi} d_{\mathrm{wu}} \left(1 + (-1)^{\mathcal{N}} e^{-i(k_z - k_z')L}\right) \delta\left(\mathbf{k}_\parallel - \mathbf{k}_\parallel'\right),$$

where

$$d_{\mathrm{wu}} = - \sum_{j=\pm1,\pm3,\pm5,\dots} \frac{a}{2\pi j} \left\langle \mathrm{w} \mid \delta U \cos\left(\frac{2\pi}{a}jz\right) \mid \mathrm{u} \right\rangle \int\limits_{-d}^{d} P'(z) \sin\left(\frac{2\pi}{a}jz\right) \mathrm{d}z; \qquad (15)$$

and

$$\mathcal{M}_{\mathrm{wv}}(\mathbf{k}, \mathbf{k}') = \frac{1}{2\pi} d_{\mathrm{wv}} \left(1 - (-1)^{\mathcal{N}} e^{-i(k_z - k_z')L}\right) \delta\left(\mathbf{k}_\parallel - \mathbf{k}_\parallel'\right),$$

where

$$d_{\mathrm{wv}} = \sum_{j=\pm1,\pm3,\pm5,\dots} \frac{a}{2\pi j} \left\langle \mathrm{w} \mid \delta U \sin\left(\frac{2\pi}{a}jz\right) \mid \mathrm{v} \right\rangle \int\limits_{-d}^{d} P'(z) \cos\left(\frac{2\pi}{a}jz\right) \mathrm{d}z. \qquad (16)$$

It can be seen that the abrupt potential of the heterointerfaces not only ensures Γ_1-X_3 [8, 17, 10], but also Γ_1-X_1 interaction [11].

We have obtained a multi-band $\mathbf{k} \cdot \mathbf{p}$ system of equations and explicit expressions for all the elements of this system required subsequently. We shall now obtain the system of three equations for the strongly interacting states Γ_1, X_1, and X_3.

2.4 Elimination of Remote Bands and Transition to r Space

In the effective-mass approximation with spatially independent effective-mass parameters, the approximate unitary transformation procedure which eliminates the influence of remote bands in the required order of perturbation theory is performed by a standard method [18], and is not given here. We obtain an integral system of equations in $\mathbf{k}$ representation. The aim of the present study is to simplify the final results as far as possible which may be achieved if the corresponding equations are differential. The problem of the accuracy of the envelope function method which occurs on transition from integral to differential equations and also when the remote bans are eliminated has already been discussed in Refs. [14, 19]. We shall summarize the constraints imposed on the accuracy of the envelope function method for this case. First, we need to determine the effective radius of the region in $\mathbf{k}$ space for which the system of equations for the envelope functions is correct (we shall call this $\mathbf{k}$ region the fundamental region). Whereas the multi-band system of equations (11) is valid for all $\mathbf{k} \in \Lambda_v$ and $\mathbf{k}' \in \Lambda_{v'}$, the unitary transformation of this system which eliminates the remote bands can, in principle, reduce the dimensions of the fundamental $\mathbf{k}$ regions. This is easily understood from the following. The spectrum of states of a bulk semiconductor $\epsilon_n^{(\mathbf{k}_0)}(\mathbf{k})$ near the point $\mathbf{k}_0$ in a band numbered n may be represented as a series in powers of $\mathbf{k}$ (for degenerate states the spectrum is determined by diagonalizing the matrix whose elements are such series). The series has a finite radius of convergence R_0, which is determined by the strength of the $\mathbf{k} \cdot \mathbf{p}$ interaction with the remote bands. This radius can be estimated as $R_0 = m_0 \bar{E}_g / (2\hbar \bar{P})$, where $\bar{E}_g$ and $\bar{P}$ are the characteristic values of the interband energy at point $\mathbf{k}_0$ and the interband matrix element of the momentum, respectively. States having quasi-momenta which do not belong to the fundamental region cannot be correctly taken into account in the transformed equation and should be neglected. We denote the corresponding radii of the fundamental $\mathbf{k}$ regions as $R_0^{(\Gamma)}$ and $R_0^{(X)}$ for conduction-band states near the points Γ and X, respectively.

Secondly, on changing from $\mathbf{k}$ to $\mathbf{r}$ representation, integration is performed over regions of $\mathbf{k}$ space of finite dimensions which prevents us from direct obtaining differential equations in $\mathbf{r}$ space. The local approximation formula involves replacing the finite regions of $\mathbf{k}$ space by infinite ones. Since the heterostructure potential is not smooth and the envelope functions obtained (or their derivatives) can vary appreciably on scales of the order of a, this procedure does not give an exponentially small error as in the case of smooth perturbations, but an error which is only small in terms of power (for this analysis it is convenient to consider the limiting case of a mathematically abrupt potential and then the envelope functions or their derivatives obtained as a result of the local approximation may have a discontinuity). Since the perturbation-theory series used for the unitary transformation is a power series, it is important to avoid the inclusion of extra-accuracy terms. For the simple single-valley case (Γ states) analyzed in detail in Ref. [19], the error of the method is of the order of $(\bar{k}_z^{(\Gamma)}/R_0^{(\Gamma)})^M$, where $1/\bar{k}_z^{(\Gamma)}$ is the characteristic length of variation of the corresponding envelope function and the exponent M is a measure of the smoothness of the latter (for an isolated heterojunction or a fairly wide quantum well $M = 3$). In this case, we need to determine two characteristic

quasi-momenta $\bar{k}_z^{(\Gamma)}$ and $\bar{k}_z^{(X)}$ for Γ and X states. In the zero-order approximation, which is acceptable for estimating the accuracy of the method, the Γ and X states do not interact and the constraint associated with the transition to differential equations is determined by the error $(\bar{k}_z^{(\Gamma)}/R_0^{(\Gamma)})^3$ for Γ states (we shall assume that the layer width L is sufficiently large so that $\bar{k}_z^{(\Gamma)}L \gtrsim 1$). For X states, the situation is slightly more complex: the system of equations for these contains both second derivatives of the envelope functions with respect to z and first derivatives as a result of $\mathbf{k} \cdot \mathbf{p}$ interaction between X_1 and X_3 bands, where the effect of this interaction may be comparable with the contribution of terms which are quadratic with respect to the momentum operator. This means that in the "worst" case, the accuracy of the local approximation for X states is limited by the error $(\bar{k}_z^{(X)}/R_0^{(\Gamma)})^2$. All these factors allow us to consider the corrections which appear as a result of the abruptness of the change in the heterointerface potential which are small as small are the parameters $a\bar{k}_z^{(\Gamma)}$ and $a\bar{k}_z^{(X)}$. Here we also note that splitting the region Λ_0 into the subregions Λ_Γ and $\tilde{\Lambda}_X$ should be performed so that $R_0^{(\Gamma)}$ and $R_0^{(X)}$ are not larger than the radii of the regions Λ_Γ and Λ_X, respectively, and then $R_0^{(\Gamma)}$ and $R_0^{(X)}$, not the radii Λ_Γ and Λ_X appear in the expressions to estimate the accuracy of the local approximation (this was implied above).

As a result, the required system of differential equations for the transformed envelope functions $\tilde{F}_m(\mathbf{r})$, where $m = \mathrm{w, u, v}$, has the following form for the strongly interacting Γ_1, X_1, and X_3 states:

$$\sum_{m'=\mathrm{w, u, v}} (T_{mm'} + V_{mm'}(z)) \tilde{F}_{m'}(\mathbf{r}) = \epsilon \tilde{F}_m(\mathbf{r}). \tag{17}$$

Here, $\mathbf{T}$ and $\mathbf{V}$ are (3×3) matrices of the kinetic and potential energies. The form of the matrix of the effective kinetic energy operator is known [20]:

$$\mathbf{T} = \begin{pmatrix} \frac{\mathbf{p}^2}{2m_\mathrm{w}} & 0 & 0 \\ 0 & \frac{\mathbf{p}_\parallel^2}{2m_{\mathrm{u}\parallel}} + \frac{\mathrm{p}_z^2}{2m_{\mathrm{u}\perp}} & \frac{(\mathrm{p}_z)_{\mathrm{uv}}\mathrm{p}_z}{m_0} + \gamma \mathrm{p}_x \mathrm{p}_y \\ 0 & \frac{(\mathrm{p}_z)_{\mathrm{vu}}\mathrm{p}_z}{m_0} + \gamma \mathrm{p}_x \mathrm{p}_y & \frac{\mathbf{p}_\parallel^2}{2m_{\mathrm{v}\parallel}} + \frac{\mathrm{p}_z^2}{2m_{\mathrm{v}\perp}} \end{pmatrix},$$

where m_w is the effective mass for Γ conduction band states, $m_{l\parallel}$ and $m_{l\perp}$ are the longitudinal and transverse effective masses for l band ($l = \mathrm{u, v}$) at point X; and the bulk parameter γ, in particular, determines the magnitude of the linear photogalvanic effect [20]. Before giving the form of the matrix of the potential energy operator, we go over from the function $P(z)$ to the function $\Theta(z) - \Theta(z - L)$ merely for the reasons of convenience [19]:

$$P(z) \approx \Theta(z) - \Theta(z - L) + \rho_0 (\delta(z) + \delta(z - L)), \tag{18}$$

where

$$\rho_0 = \int\limits_{-d}^{d} P(z)\, \mathrm{d}z - d.$$

Now the matrix of the effective potential energy operator $\mathbf{V}$ may be expressed as the sum of three matrices: $\mathbf{V}_1 + \mathbf{V}_2 + \mathbf{V}_3$. The diagonal matrix $\mathbf{V}_1$ corresponds to the standard (bulk) effective-mass approximation [18]:

$$(V_1)_{ss'} = \{\epsilon_{ss'} + \delta U_{ss'}[\Theta(z) - \Theta(z-L)]\}\delta_{ss'}.$$

As a result of the abruptness of the heterointerface potential, the matrix $\mathbf{V}_2$ contains both intravalley contributions and contributions which mix X_1 and X_3 states (all the parameters $d_{mm'}$ are real):

$$\mathbf{V}_2 = \begin{pmatrix} \tilde{d}_{\mathrm{ww}}(\delta(z) + \delta(z-L)) & 0 & 0 \\ 0 & \tilde{d}_{\mathrm{uu}}(\delta(z) + \delta(z-L)) & d_{\mathrm{uv}}(\delta(z) - \delta(z-L)) \\ 0 & d_{\mathrm{uv}}(\delta(z) - \delta(z-L)) & \tilde{d}_{\mathrm{vv}}(\delta(z) + \delta(z-L)) \end{pmatrix}.$$

Here, the parameters $\tilde{d}_{\mathrm{ss}}$ are related to d_{ss} as follows:

$$\tilde{d}_{\mathrm{ss}} = d_{\mathrm{ss}} + \delta U_{\mathrm{ss}}\rho_0.$$

Finally, the matrix $\mathbf{V}_3$ contains contributions which mix Γ and X_z states (also as a result of the abruptness of the heterointerface potential). We give the non-zero elements of $\mathbf{V}_3$:

$$(V_3)_{\mathrm{wu}} = (V_3)_{\mathrm{uw}} = d_{\mathrm{wu}}\left(\delta(z) + (-1)^{\mathcal{N}}\delta(z-L)\right), \tag{19}$$

$$(V_3)_{\mathrm{wv}} = (V_3)_{\mathrm{vw}} = d_{\mathrm{wv}}\left(\delta(z) - (-1)^{\mathcal{N}}\delta(z-L)\right). \tag{20}$$

In our approximation, the expression linking the envelope functions and the complete wave function has the usual form (we again drop the valley index):

$$\Psi(\mathbf{r}) = \sum_{m=\mathrm{w,\,u,\,v}}\left[\tilde{F}_m(\mathbf{r})\phi_m + {\sum_n}'\frac{\hbar\mathbf{p}_{nm}\cdot\left(\boldsymbol{\nabla}\tilde{F}_m(\mathbf{r})\right)}{im_0(\epsilon_m - \epsilon_n)}\phi_n\right].$$

For an arbitrary number of heterojunctions at $z = z_j$ numbered by the index j, the nonzero elements of $\mathbf{V}_3$ may be written in the following form:

$$(V_3)_{\mathrm{wu}} = (V_3)_{\mathrm{uw}} = \sum_j e^{iqz_j}d_{\mathrm{wu}}^{(j)}\delta(z - z_j),$$

$$(V_3)_{\mathrm{wv}} = (V_3)_{\mathrm{vw}} = \sum_j e^{iqz_j}d_{\mathrm{wv}}^{(j)}\delta(z - z_j),$$

where q is the distance in $\mathbf{k}$ space between the centers of the valleys under consideration (in our case, $q = (0, 0, 2\pi/a)$). Since the parameters $d_{\mathrm{wu}}^{(j)}$ and $d_{\mathrm{wv}}^{(j)}$ depend not only on the heterojunction materials but also on the microscopic structure of the interface, these must generally be determined for each interface separately.

3 Discussion of Results and Conclusions

Using $\mathbf{k} \cdot \mathbf{p}$ formalism, we have constructed a generalization of the method of envelope functions suitable to describe the interaction of Γ and X_z states in (001) III-V nanostructures formed from related lattice-matched semiconductors. In the derived system of equations (17), mixing of the states of different valleys is determined by the heterosurface effective potentials (19) and (20), similar to those introduced phenomenologically in Ref. [6]. The system (17) contains information on the number $\mathcal{N}$ of monoatomic layers of the structure. An oscillatory dependence of the effective intervalley mixing strength on $\mathcal{N}$ was obtained, in particular, in Ref. [7], and was also introduced from symmetry concepts (in terms of the boundary conditions for the envelope functions) in Ref. [17]. However, in addition to this, there are some difference between the results of the present study and the results of other authors. The most important of these is the appearance of direct interaction between Γ_1 and X_1 states whose strength is determined by the parameter d_{wu}. This was predicted recently in Refs. [11, 15, 16]. The strength of Γ_1-X_1 interaction, i.e., the value of the constant d_{wu}, depends strongly on the structure of the heterointerface on atomic scales. In simplified models, such as the simplest variants of the tight-binding method, this interaction may be absent. It is clear from (15) that in the hypothetical case of mathematically abrupt heterojunctions when $P(z) = \Theta(z) - \Theta(z - L)$, we in fact find $d_{\mathrm{wu}} = 0$. The conclusion reached in Ref. [10] that $d_{\mathrm{wu}} \ll d_{\mathrm{wv}}$ was specifically a consequence of the selected heterojunction model for which the simplest case is a mathematically abrupt jump (see also Ref. [11]). In general, there is no basis for assuming that d_{wu} differs substantially from d_{wv}, and since X_1 band is lower in energy than X_3 one, the existence of Γ_1-X_1 interaction may be very significant for interpreting experiments.

In Ref. [19] we considered a more complex model of the potential of an ideal heterostructure and, specifically, took into account a periodic coordinate dependence of the heterostructure form-factor in the (001) plane. We showed that this complication merely leads to renormalization of some parameters obtained using (2). However, whereas it was found using the simple form-factor model that the mixing strength of the heavy and light holes at the center of the 2D Brillouin zone was higher for abrupt heterojunctions than for structures with a continuously varying composition, this conclusion was not obtained using the more complex form-factor model. We could merely conclude that the strength of the light hole-heavy hole mixing depended on the structure of the transition region of the heterointerfaces. Having made a similar analysis for our case, we can easily show that Γ-X mixing strength in fact depends strongly on how abruptly (on scales of the order a) the chemical composition at the heterojunction varies. This conclusion which follows directly from expressions (15) and (16) for the parameters d_{wu} and d_{wv} is quite natural since transitions with such a large (of the order of the dimensions of the Brillouin zone) change in the quasi-momentum k_z can only be achieved by electron scattering at an atomically abrupt heterointerface (in formal terms the Fourier components of the heterointerface potential with the wave vectors close to $k_z = 2\pi/a$ are responsible for Γ-X transitions).

Acknowledgements

References

[1] R. Teissier, J. J. Finley, M. S. Skolnick, J. W. Cockburn, J.-L. Pelouard, R. Grey, G. Hill, M. A. Pate, and R. Planel, Phys. Rev. **B54**, R8329 (1996).

[2] Yu. N. Khanin, E. E. Vdovin, Yu. V. Dubrovskii, K. S. Novoselov, and T. G. Andersson, Pis'ma Zh. Eksp. Teor. Fiz. **67**, 814 (1998) [JETP Lett. **67**, 863 (1998)].

[3] M. Nakayama, K. Imazawa, K. Suyama, I. Tanaka, and H. Nishimura, Phys. Rev. **B49**, 13564 (1994).

[4] N. Ohtani, M. Hosoda, H. Mimura, K. Tominaga, and T. Watanabe, Jpn. J. Appl. Phys. **36**, 1884 (1997).

[5] O. E. Raichev, Phys. Rev. **B49**, 5448 (1994).

[6] H. C. Liu, Appl. Phys. Lett. **51**, 1019 (1987).

[7] Yan-Ten Lu and L. J. Sham, Phys. Rev. **B40**, 5567 (1989).

[8] T. Ando and H. Akera, Phys. Rev. **B40**, 11619 (1989).

[9] A. Franceschetti and A. Zunger, Phys. Rev. **B52**, 14664 (1995).

[10] B. A. Foreman, Phys. Rev. Lett. **81**, 425 (1998).

[11] P. C. Klipstein, in *Proceedings of the 24th International Conference on The Physics of Semiconductors*, Jerusalem, 1998, edited by M. Heiblum and E. Cohen (World Sci., Singapore, 1999), CDROM file: 1265.pdf.

[12] J. N. Schulman, J. Vac. Sci. Technol. **B1**, 644 (1983).

[13] F. Bassani and G. Pastori Parravicini, *Electronic states and optical transitions in solids* (Pergamon, New York, 1975; Nauka, Moscow, 1982).

[14] V. A. Volkov and E. E. Takhtamirov, Usp. Fiz. Nauk **167**, 1123 (1997) [Physics-Uspekhi **40**, 1071 (1997)].

[15] V. A. Volkov and E. E. Takhtamirov, in *Proceedings of the III All-Russia Conference on the Physics of Semiconductors, "Poluprovodniki'97"* (Fiz. Inst. Akad. Nauk, Moscow, 1997), p. 127.

[16] E. E. Takhtamirov, *Candidate's Dissertation* (Moscow, 1998).

[17] Y. Fu, M. Willander, E. L. Ivchenko, and A. A. Kiselev, Phys. Rev. **B47**, 13498 (1993).

[18] J.M. Luttinger, W. Kohn, Phys. Rev. **97**, 869 (1955).

[19] E. E. Takhtamirov and V. A. Volkov, Zh. Eksp. Teor. Fiz. **116**, 1843 (1999) [JETP **89**, 1000 (1999)].

[20] E. L. Ivchenko and G. E. Pikus, Fiz. Tekh. Poluprovodn. (Leningrad) **13**, 992 (1979) [Sov. Phys. Semicond. **13**, 579 (1979)].